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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

ATTY.'S DOCKET: HARTAL=1B

In re Application of:	)	Art Unit: 1761
	)	
Dov HARTAL et al	)	Examiner: C. Sherrer
	)	
Appln. No.: 09/449,093	)	Washington, D.C.
	)	
Date Filed: November 24, 1999	)	Confirmation No. 5856
	)	
For: NATURAL COLORING PRODUCTS	)	August 1, 2003

SUBMISSION OF DOCUMENTARY EVIDENCE IN SUPPORT OF  
DECLARATION OF DR. HARTAL

Honorable Commissioner for Patents  
2011 South Clark Place  
Mail Stop \_\_\_\_\_  
Crystal Plaza Two, Lobby, Room 1B03  
Arlington, VA 22202

Sir:

Attached are documents in support of the Declaration of Dr. Hartal under 37 CFR 1.132 executed May 27, 2003, and filed in the PTO on June 10, 2003, with a Reply erroneously dated June 4, 2003. The evidentiary documents filed herewith are the following:

1. Pages 22 and 23 from a document headed "USDA - NCC Carotenoid Database for U.S. Foods-1998":

Page 22, item 11886 shows the lycopene content of canned tomato juice to be 93.18.

The next item 11887 shows the lycopene content of canned tomato paste to be 293.3.

On the next page, page 23, the first item 11529 discloses the lycopene content of average year around, raw, ripe, red tomatoes to be 30.25.

2. The next pages attached are pages 78 and 79 of a document setting forth 21 CFR 101.30 entitled "Percentage Juice Declaration for Foods Purporting to be Beverages That Contain Fruit or Vegetable Juice." Page 79 contains a table of 100% juices indicating that the Brix value of tomato juice is 5.0.

3. The next document includes a title page and pages 2 and 4 from a document entitled "Tomato Paste" by Peter Goose et al. The table on page 4 sets forth the solid contents, degree of concentration, estimated by determination of refractometer solids of products running from light tomato puree to heavy tomato paste, these values being 11 to 45. Undersigned understands that these values are equivalent or roughly equivalent to the Brix values for these commercial products.

4. Two other documents are enclosed, a first entitled "Kinetics of Colour of Double Concentrated Tomato Paste During Thermal Treatment" by Barreiro et al, and the second bearing the title "White Book on the Antioxidants in Tomatoes and Tomato Products and Their Health Benefits", final report of the Concerted Action FAIR CT97-3233. These two

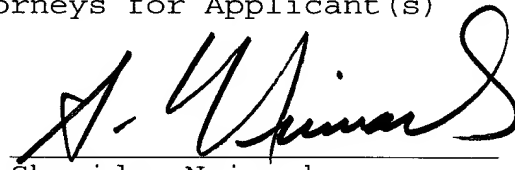
documents confirm the damaging effects of heat treatment on lycopene. As argued extensively, previously, the claimed process which avoids the damaging effects of heat treatment, which heat treatment is prevalent in the prior art, thus avoids substantial destruction of the chromoplasts.

Applicants request consideration of these documents, along with the Reply and Dr. Hartal's Declaration, both filed June 10, 2003, and applicants again respectfully requests favorable reconsideration and allowance.

Respectfully submitted,

BROWDY AND NEIMARK, P.L.L.C.  
Attorneys for Applicant(s)

By



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# USDA-NCC Carotenoid Database for U. S. Foods - 1998

(Units= $\mu\text{g}/100\text{g}$  edible portion for Mean, SEM, Min, and Max; #S = is the total number of means/individual values)

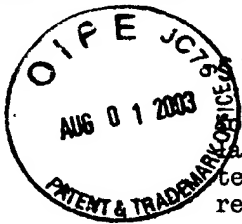
NDB	Desc	Carot	Mean	SEM	#S	Min	Max	CC	Ref. No.
11886	Tomato juice, canned, without salt added	a_car	0		1			c	41
		b_car	428		2	270	900	b	8,41
		b_cryp	0		1			c	41
		lut + zea	60		1			c	41
		lyc	9,318	1,269	5	5,000	11,600	a	1,8,41
11887	Tomato products, canned, paste, with salt added	a_car	29	35	3	0	200	b	8,9,41
		b_car	1,242	206	3	910	1,700	b	8,9,41
		b_cryp	0		2	0	0	b	9,41
		lut + zea	170		2	0	340	b	9,41
		lyc	29,330	10,860	5	5,400	55,450	a	8,9,41
11888	Tomato products, canned, puree, with salt added	a_car	0		1			c	41
		b_car	410		1			c	41
		b_cryp	0		1			c	41
		lut + zea	90		1			c	41
		lyc	16,670		1			c	41
11549	Tomato products, canned, sauce	a_car	0		2	0	0	b	9,41
		b_car	410		2	370	450	b	9,41
		b_cryp	0		2	0	0	b	9,41
		lut + zea	1		2	0	2	b	9,41
		lyc	15,916	1,829	3	7,300	17,980	b	8,9,41
11530	Tomatoes, red, ripe, cooked, boiled, without salt	a_car	0		1			c	23
		b_car	300		1			c	23
		b_cryp	0		1			c	23
		lut + zea	150		1			c	23
		lyc	4,400		1			c	23
11531	Tomatoes, red, ripe, canned, whole, regular pack	a_car	0		2	0	0	b	9,41
		b_car	186	43	3	70	230	b	9,10,41
		b_cryp	0		2	0	0	b	9,41
		lut + zea	40		2	0	80	b	9,41
		lyc	9,708		2	9,270	10,145	b	9,41

# USDA-NCC Carotenoid Database for U. S. Foods - 1998

23

(Units= $\mu$ g/100g edible portion for Mean, SEM, Min, and Max; #S = is the total number of means/individual values)

NDB	Desc	Carot	Mean	SEM	#S	Min	Max	CC	Ref. No.
11529	Tomatoes, red, ripe, raw, year round average	a_car	112		2	0	223	c	6,23
		b_car	393	71	7	115	700	a	6,8,11,23,30,48
		b_cryp	0		1			c	23
		lut + zea	130		1			c	23
		lyc	3,025	596	5	879	4,200	a	8,23,48
11569	Turnip greens, cooked, boiled, drained, without salt	a_car	0		1			c	9
		b_car	4,575		1			c	9
		b_cryp	0		1			c	9
		lut + zea	8,440		1			c	9
		lyc	0		1			c	9
11996	Vegetable combination with butter sauce (broccoli, cauliflower and baby carrot)	a_car	333		1			c	9
		b_car	450		1			c	9
		b_cryp	0		1			c	9
		lut + zea	142		1			c	9
		lyc	0		1			c	9
22509	Vegetables (includes white potatoes, sweet potatoes, rutabagas, green beans, and onions) with beef and sauce, low fat frozen entree, cooked	a_car	0		1			c	9
		b_car	352		1			c	9
		b_cryp	0		1			c	9
		lut + zea	70		1			c	9
		lyc	285		1			c	9
11578	Vegetable juice cocktail, canned	a_car	210		1			c	41
		b_car	830		1			c	41
		b_cryp	0		1			c	41
		lut + zea	80		1			c	41
		lyc	9,660		1			c	41
11990	Wasabi, root, raw	a_car	0		1			c	43
		b_car	14		1			c	43
		b_cryp	0		1			c	43



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21 CFR Ch. I (4-1-01 Edition)

for the color additive. Voluntary declaration of all colorings added to butter, cheese, and ice cream, however, is recommended.

[42 FR 14308, Mar. 15, 1977, as amended at 44 FR 3963, Jan. 19, 1979; 44 FR 37220, June 26, 1979; 54 FR 24891, June 12, 1989; 58 FR 2875, Jan. 6, 1993; 63 FR 14818, Mar. 27, 1998]

**\$101.30 Percentage juice declaration for foods purporting to be beverages that contain fruit or vegetable juice.**

(a) This section applies to any food that purports to be a beverage that contains any fruit or vegetable juice (i.e., the product's advertising, label, or labeling bears the name of, or variation on the name of, or makes any other direct or indirect representation with respect to, any fruit or vegetable juice), or the label or labeling bears any vignette (i.e., depiction of a fruit or vegetable) or other pictorial representation of any fruit or vegetable, or the product contains color and flavor that gives the beverage the appearance and taste of containing a fruit or vegetable juice. The beverage may be carbonated or noncarbonated, concentrated, full-strength, diluted, or contain no juice. For example, a soft drink (soda) that does not represent or suggest by its physical characteristics, name, labeling, ingredient statement, or advertising that it contains fruit or vegetable juice does not purport to contain juice and therefore does not require a percent juice declaration.

(b)(1) If the beverage contains fruit or vegetable juice, the percentage shall be declared by the words "Contains \_\_\_ percent (or %) \_\_\_ juice" or "\_\_\_ percent (or %) juice," or a similar phrase, with the first blank filled in with the percentage expressed as a whole number not greater than the actual percentage of the juice and the second blank (if used) filled in with the name of the particular fruit or vegetable (e.g., "Contains 50 percent apple juice" or "50 percent juice").

(2) If the beverage contains less than 1 percent juice, the total percentage juice shall be declared as "less than 1 percent juice" or "less than 1 percent \_\_\_ juice" with the blank filled in with the name of the particular fruit or vegetable.

(3) If the beverage contains 100 percent juice and also contains non-juice ingredients that do not result in a diminution of the juice soluble solids or, in the case of expressed juice, in a change in the volume, when the 100 percent juice declaration appears on a panel of the label that does not also bear the ingredient statement, it must be accompanied by the phrase "with added \_\_\_\_\_," the blank filled in with a term such as "ingredient(s)," "preservative," or "sweetener," as appropriate (e.g., "100% juice with added sweetener"), except that when the presence of the non-juice ingredient(s) is declared as a part of the statement of identity of the product, this phrase need not accompany the 100 percent juice declaration.

(c) If a beverage contains minor amounts of juice for flavoring and is labeled with a flavor description using terms such as "flavor," "flavored," or "flavoring" with a fruit or vegetable name and does not bear:

(1) The term "juice" on the label other than in the ingredient statement; or

(2) An explicit vignette depicting the fruit or vegetable from which the flavor derives, such as juice exuding from a fruit or vegetable; or

(3) Specific physical resemblance to a juice or distinctive juice characteristic such as pulp then total percentage juice declaration is not required.

(d) If the beverage does not meet the criteria for exemption from total juice percentage declaration as described in paragraph (c) of this section and contains no fruit or vegetable juice, but the labeling or color and flavor of the beverage represents, suggests, or implies that fruit or vegetable juice may be present (e.g., the product advertising or labeling bears the name, a variation of the name, or a pictorial representation of any fruit or vegetable, or the product contains color and flavor that give the beverage the appearance and taste of containing a fruit or vegetable juice), then the label shall declare "contains zero (0) percent (or %) juice". Alternatively, the label may declare "Containing (or contains) no \_\_\_ juice", or "no \_\_\_ juice", or "does not contain \_\_\_ juice", the blank to be filled in with the name of

the fruits or vegetables represented, suggested, or implied, but if there is a general suggestion that the product contains fruit or vegetable juice, such as the presence of fruit pulp, the blank shall be filled in with the word "fruit" or "vegetable" as applicable (e.g., "contains no fruit juice", or "does not contain fruit juice").

(e) If the beverage is sold in a package with an information panel as defined in §101.2, the declaration of amount of juice shall be prominently placed on the information panel in lines generally parallel to other required information, appearing:

(1) Near the top of the information panel, with no other printed label information appearing above the statement except the brand name, product name, logo, or universal product code; and

(2) In easily legible boldface print or type in distinct contrast to other printed or graphic matter, in a height not less than the largest type found on the information panel except that used for the brand name, product name, logo, universal product code, or the title phrase "Nutrition Facts" appearing in the nutrition information as required by §101.9.

(f) The percentage juice declaration may also be placed on the principal display panel, provided that the declaration is consistent with that presented on the information panel.

(g) If the beverage is sold in a package that does not bear an information panel as defined in §101.2, the percentage juice declaration shall be placed on the principal display panel, in type size not less than that required for the declaration of net quantity of contents statement in §101.105(i), and be placed near the name of the food.

(h)(1) In enforcing these regulations, the Food and Drug Administration will calculate the labeled percentage of juice from concentrate found in a juice or juice beverage using the minimum Brix levels listed below where single-strength (100 percent) juice has at least the specified minimum Brix listed below:

Juice	100 percent juice <sup>1</sup>
Acerola .....	6.0

Juice	100 percent juice <sup>1</sup>
Apple .....	11.5
Apricot .....	11.7
Banana .....	22.0
Blackberry .....	10.0
Blueberry .....	10.0
Boysenberry .....	10.0
Cantaloupe Melon .....	9.6
Carambola .....	7.8
Carrot .....	8.0
Casaba Melon .....	7.5
Cashew (Caju) .....	12.0
Celery .....	3.1
Cherry, dark, sweet .....	20.0
Cherry, red, sour .....	14.0
Crabapple .....	15.4
Cranberry .....	7.5
Currant (Black) .....	11.0
Currant (Red) .....	10.5
Date .....	18.5
Dewberry .....	10.0
Elderberry .....	11.0
Fig .....	18.2
Gooseberry .....	8.3
Grape .....	16.0
Grapefruit .....	10.0
Guanabana (soursop) .....	16.0
Guava .....	7.7
Honeydew melon .....	9.6
Kiwi .....	15.4
Lemon .....	4.5
Lime .....	4.5
Loganberry .....	10.5
Mango .....	13.0
Nectarine .....	11.8
Orange .....	11.8
Papaya .....	11.5
Passion Fruit .....	14.0
Peach .....	10.5
Pear .....	12.0
Pineapple .....	12.8
Plum .....	14.3
Pomegranate .....	16.0
Prune .....	18.5
Quince .....	13.3
Raspberry (Black) .....	11.1
Raspberry (Red) .....	9.2
Rhubarb .....	5.7
Strawberry .....	8.0
Tangerine .....	11.8
Tomato .....	5.0
Watermelon .....	7.8
Youngberry .....	10.0

<sup>1</sup> Indicates Brix value unless other value specified.

<sup>2</sup> Indicates anhydrous citrus acid percent by weight.

<sup>3</sup> Brix values determined by refractometer for citrus juices may be corrected for citric acid.

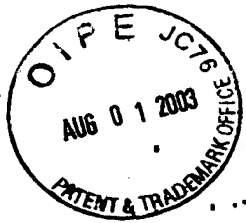
(2) If there is no Brix level specified in paragraph (h)(1) of this section, the labeled percentage of that juice from concentrate in a juice or juice beverage will be calculated on the basis of the soluble solids content of the single-strength (unconcentrated) juice used to produce such concentrated juice.

(i) Juices directly expressed from a fruit or vegetable (i.e., not concentrated and reconstituted) shall be considered to be 100 percent juice and shall be declared as "100 percent juice."

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# TOMATO PASTE

PURÉE. JUICE & POWDER

BY

PETER G. GOOSE. A.R.I.C.. A.I.L.(R)

&

RAYMOND BINSTED



parts of Southern Europe by peasant families—were doubtless the beginnings of the present day tomato paste industry.

### *Tomato Paste.*

Tomato paste is the product resulting from the concentration by evaporation of water from pulped tomatoes, after the removal of skins and seeds. In present day commerce it usually represents a concentrate in which the tomato solids have been increased from the natural 5–6% (in the fresh fruit) to 28–30% (double concentrate) or 36–40% (triple concentrate). Less commonly, solids contents from 11% to 45% may be encountered and, with the improved modern methods of evaporation of syrup after centrifuging, even higher solids contents are becoming commercially available. The Comité International Permanent de la Conserve (C.I.P.C.) have introduced a suggested nomenclature for tomato concentrates, which is as given later in this chapter.

The standard concentration in California for tomato paste was, for many years, 26% solids, and the term 'paste' rather than 'purée' was used for the higher concentrations. Today both terms are used almost synonymously and in some quarters the material is known as 'tomato concentrate'. Throughout this book the term 'paste' will be used to signify all tomato pulp which has been subjected to a concentration process. Tomato pulp means the crushed tomatoes, either before or after the removal of skins and seeds. Tomato juice means the crushed, screened and refined tomato pulp in an unconcentrated condition as the base of a beverage. Tomato 'serum' means the filtered juice or pulp. Completely dehydrated tomato paste forms 'tomato powder'.

The terms 'double' and 'triple', as used in describing tomato pastes, are not literal and, in fact, double concentrate yields approximately one-fifth, and triple concentrate one-sixth, the weight of raw pulp—and somewhat less when related to the original weight of fruit before removal of skins and seeds.

The equivalent phrases for tomato paste in the principal European languages are as follows:

Italian	Concentrato di pomodoro
Spanish	Concentrado de tomate
German	Tomaten mark
French	Extrait des tomates (Purée des tomates)

The standards of quality which have been established for tomato paste in various countries are largely based on the standards issued

*Article 1—Definition.*

1. The terms 'tomato purée' and 'tomato paste', accompanied by the words 'light', 'medium' or 'heavy' in accordance with the degrees of concentration as hereafter defined, apply to the canned products prepared by straining the fresh fruit of the tomato '*Lycopersicum esculentum* L.' and concentrating, thereby removing part of the water, the resulting pulpy liquid.

2. According to the degree of concentration, estimated by determination of the refractometer solids (less added salt) as set out in Article 4, the products listed in paragraph 1. above, are described as follows:

*Minimum percentage  
of refractometer solids  
(less added salt)*

*Description*

11	Light tomato purée, minimum solids 11 per cent.
15	Medium tomato purée, minimum solids 15 per cent.
22	Heavy tomato purée, minimum solids 22 per cent.
28	Light tomato paste, minimum solids 28 per cent.
36	Medium tomato paste, minimum solids 36 per cent.
45	Heavy tomato paste, minimum solids 45 per cent.

The minimum percentage of solids, corresponding to the degree of concentration in accordance with the list given above, shall be stated on the label, immediately following the name of the product and given as a single number written in the same type, as follows: 'minimum solids: x %'.

The sale of tomato purées containing less than 11 per cent solids is not permitted. This prohibition does not however apply to tomato juice, nor to tomato soups, sauces, seasonings or pickles.

The percentage of solids shall always be given less added salt, that is to say minus the quantity of salt which has been added to the product, corrected for the natural chlorides present in the tomato, which are arbitrarily rated as amounting to 2 per cent of the solids.

3. The tomato purées and pastes defined above may be sold either without any statement of quality (standard quality) or with the statement 'extra quality'. They should satisfy the requirements set forth in Article 3.

No other description is permitted.



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## Kinetics of Colour Change of Double Concentrated Tomato Paste During Thermal Treatment

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(Received 20 December 1995; accepted 18 May 1997)

### ABSTRACT

The kinetics of the colour change of double concentrated tomato paste during heating was studied. The Hunter 'L', 'a', 'b' tristimulus values were measured to characterise the colour, and colour difference ( $\Delta E$ ); saturation index (SI) and 'a/b' ratio were calculated from those values. The kinetic study was performed using the capillary tube method with temperatures ranging from 70.0 to 100.0°C. The order of reaction and the constants  $E_a$  and  $k_0$  of the Arrhenius equation were determined. All the colour parameters followed an apparent first order kinetics, with the exception of  $\Delta E$ , which showed a zero order behaviour. The degradation of the colour parameter 'L' followed two consecutive first order reactions, with  $E_a$  values of 11.5 and 5.73 kcal mol<sup>-1</sup>, and  $\ln k_0$  of 11.3 and 1.28 min<sup>-1</sup> for both phases, respectively. The parameter 'b' ( $E_a$  = 20.5 kcal mol<sup>-1</sup>;  $\ln k_0$  = 22.2 min<sup>-1</sup>) was more sensitive to temperature changes than the parameter 'a' ( $E_a$  = 9.79 kcal mol<sup>-1</sup>;  $\ln k_0$  = 9.10 min<sup>-1</sup>), and other colour parameters. The 'a/b' ratio showed an  $E_a$  = 6.86 kcal mol<sup>-1</sup> ( $\ln k_0$  = 5.20 min<sup>-1</sup>), smaller than that of all the other colour parameters, with the exception of 'L' (second phase). Thus, 'a/b' was less sensitive to changes during heating than most of the other parameters. Values of  $E_a$  and  $\ln k_0$  of 10.2 kcal mol<sup>-1</sup> and 12.9 min<sup>-1</sup> for  $\Delta E$ , and 10.1 kcal mol<sup>-1</sup> and 9.28 min<sup>-1</sup> for SI were determined. The parameters obtained permit colour change prediction in double concentrated tomato paste during thermal processing. © 1997 Elsevier Science Limited. All rights reserved

\*To whom all correspondence should be addressed.

## INTRODUCTION

The thermal processing of food is primarily intended to inactivate pathogens and other deteriorative microorganisms capable of making it unsuitable for consumption. At the same time, it has an inactivation effect on enzymatic systems, nutrients, and organoleptic properties, including texture and colour.

Colour is a very important quality factor in processed tomato products, particularly tomato concentrates, since it influences consumer acceptability. There are many reactions that can take place during thermal processing that affect colour. Among them, the most common are pigment degradation, especially carotenoids (lycopene, xanthophyll, etc.) and chlorophyll, and browning reactions such as the Maillard reaction and oxidation of ascorbic acid (Bontovits, 1981; Mauron, 1981). In tomato products, an important reaction is the degradation of the red pigment lycopene, originally in the *trans* form, that isomerises to the *cis* structure during heating, resulting in changes in colour. Additionally, the presence of residual chlorophyll that could be present in the juice as the result of grinding nonripe tomatoes for its manufacture, is converted to pheophytin of olive green colour (Narkiroj & Ranganna, 1977; Schwartz & Von Elbe, 1983; Schwartz & Lorenzo, 1990). The degradation of colour during heating of tomato products actually involves a series of complex reactions whose mechanisms and modes of action are presently not completely understood.

Colour is usually defined by three coordinates. There are various colour scales that can be used to characterise colour: CIE-X,Y,Z; the 'L', 'a', 'b'; and the  $R_d$ ,  $a$ ,  $b$  scales. Similarly, colour indexes and differences can be calculated from these values. The 'L', 'a', 'b' scale is recognised to show a better discrimination between small colour differences in the darker region of the colour space, providing good discrimination for saturated colours, as in the case of tomato products. For these reasons this scale is one of the most frequently used for food products (Francis, 1989), however, it is not so useful for light coloured samples (Anon., 1976).

The 'L' value represents a nonlinear mathematical approximation of the white-black response of the eye, ranging from 100 for a perfect white to 0 for a perfect black, and measures the luminosity of the sample. A positive value of 'a' indicates redness, and a negative value greenness. A plus value for 'b' indicates yellowness and a minus value blueness. There are other parameters derived from the Hunter-'L', 'a', 'b' scale: the total colour difference ( $\Delta E$ ), the saturation index (SI) or chroma that indicates colour saturation and is proportional to its intensity, 'a/b' ratio and the Hue angle among others (Francis & Clydesdale, 1975; Little, 1975; Anon., 1976; Abers & Wrolstad, 1979; Puppo-Ferreira, 1981; Francis, 1989). The 'a/b' ratio has been used as a quality specification for tomato products. Values of 2.0 and above are indicative of an excellent colour in tomato paste, while a value below 1.80 is considered unacceptable (Goose & Binsted, 1973; Anon., 1976). The Hue angle ( $\tan^{-1} b/a$ ) is another parameter frequently used to characterise colour in food products. An angle of 0 or 360° represents red Hue, while angles of 90, 180 and 270° represent yellow, green and blue Hue, respectively. It has been extensively used in the evaluation of colour parameters in green vegetables, fruits and meats.

Most of the quality factors, including colour, can be described by a degradation kinetics of zero or first order, with the effect of temperature in the velocity constant taken into account by the Arrhenius equation (Lund, 1975; Kessler & Fink, 1986; Wells & Singh, 1988; Rhim *et al.*, 1989a). Most of the kinetic analyses and studies

found in the literature for the change of colour by effect of heat in foods have been done in milk and some fruit juices (Rhim *et al.*, 1988a,b, 1989a,b; Pagliarini *et al.*, 1990). No kinetic studies related with the colour degradation of tomato concentrates during thermal processing were found in the literature. The objective of this research work was to study the kinetics of colour degradation by heat in double concentrated tomato paste in order to predict colour changes with temperature during thermal processing.

## MATERIALS AND METHODS

### Sample collection

Tomato samples of double concentrated tomato paste used in this study were collected during the tomato harvest season of 1992, in a commercial plant in Venezuela. The samples were drawn after the concentration process and before thermal processing for hot-filling. The plant used a cold-break rupture process. All samples used were from the same lot. About 15 l of tomato paste were sampled. The samples were kept in glass jars under refrigeration (about 4 to 7°C), protected from light with aluminium foil, and properly closed until used for the experiments.

### Physical and chemical characteristics of tomato paste

The following analyses were done to characterise the double concentrated tomato paste used in this study: soluble solids (°Brix), corrected for temperature and acidity (NCA, 1968; Goose & Binsted, 1973), employing an Abbé refractometer (Bausch and Lomb, model 3-E); moisture: utilising a vacuum oven procedure at 70°C (AOAC, 1990); water activity ( $a_w$ ) at 23°C using a psychometric equipment (Decagon CX-1); acidity: by electrometric titration (NCA, 1968; Goose & Binsted, 1973); pH: with a Ph meter (Bantex-300A) (NCA, 1968).

### Colour analysis

After mixing the samples carefully, the determination of the colour parameters was done using a tristimulus colorimeter (Gardner XL-23) with the scales 'L', 'a', 'b'. The equipment was calibrated against a red tile standard No. CG-6802 GCS-1 with the following colour parameters: 'L' = 28.3; 'a' = +49.6; 'b' = +16.4. A 10 ml cell was used for the sample. The parameters 'L', 'a' and 'b' of the sample were read and the values of  $\Delta E$ , SI, 'a/b', and Hue angle were calculated.

Colour difference  $\Delta E$  was determined from the colour parameters of control nonheated samples and heated samples, and the values of SI and 'a/b' from the parameters read using the equations presented by Francis and Clydesdale (1975), Anon. (1976), Abers and Wrolstad (1979), Puppo-Ferreira (1981) and Little (1975).

$$\Delta E = \sqrt{(L_0 - L)^2 + (a_0 - a)^2 + (b_0 - b)^2} \quad (1)$$

$$SI = \sqrt{a^2 + b^2} \quad (2)$$

$$\text{Hue angle} = \tan^{-1} b/a \quad (3)$$

where  $L_0$ ,  $a_0$  and  $b_0$  denote the colour parameters for the control samples (unheated);  $L$ ,  $a$  and  $b$  denote the colour parameters of the heated samples.

### Kinetic studies for the change of colour during heating

To study the change of colour during heating, a modified capillary tube method similar to that described by Stumbo (1973) was followed. For this purpose and due to the difficulty of filling capillary tubes with tomato paste, Pyrex glass vials of about 9 ml in volume (total length: 59.3 mm; inner diameter: 13.5 mm; wall thickness: 2.0 mm), provided with bakelite screw caps were used. The vials were filled with 8.0 ml of sample, taking care to avoid incorporation of air bubbles and were closed. A total of 5 vials were used for each time period. All trials were done in triplicate. Therefore, a total of 15 vials were used for each time-temperature treatment.

For the heat treatment of the samples, time-temperature relationships applied included values in which the change of colour was visually evidenced. Temperatures of 70.0, 80.0, 90.0 and 100.0°C were selected. For the first three temperatures a thermostatic water bath (Blue-M-Magni Whirl,  $\pm 0.1^\circ\text{C}$ ) was used, while for the temperature of 100.0°C a thermostatic bath using motor oil (Precision Scientific,  $\pm 0.01^\circ\text{C}$ ) was employed. The heating time ranged from 5 to 90 min. After the heat treatment was applied the vials were removed and transferred to a cold water bath with crushed ice (about 2–3°C) in order to stop the heat treatment.

Due to the amount of product that had to be used, the samples were pre-heated in a microwave oven (Tappan 2450 MHz) to hasten heating to a temperature near to that of the experiment, and reduce the transient heat transfer process. In order to establish the heating time, a trial and error procedure was followed to determine the period to reach the temperature of the experiment within a range of about 2°C. The temperature was measured, after the samples were removed from the oven, introducing in the vials copper-constantan (Type T) thermocouples (Ellab, model 7667) using a Speedomax 2500 (Leeds and Northrup) equipment. In this way the error in the sample come-up time, after introduction in the bath, was minimised.

The heating time was measured from the moment the samples reached the processing temperature until they were introduced in the cold water bath, using a chronometer (Excelsior Park,  $\pm 0.5$  s). In order to determine the sample temperature a needle copper-constantan thermocouple, type T (Ellab, model 7667, 1 mm diameter), placed in the geometrical centre of the vials was used in junction with a time-temperature recorder (Leeds and Northrup, model Speedomax 2500,  $\pm 1^\circ\text{F}$ ).

Once the samples (quintuplicates) were heated and cooled at the established time and temperature, they were carefully mixed in a composite sample, in order to have enough quantity to allow the measurement of the colour parameters in the colorimeter as indicated previously.

The apparent order of reaction for the colour parameters was determined by the adjustment of the experimental data to the integrated kinetic equations for orders 0, 1 and 2, using regression analysis. In each case the best fit was selected and the constant of velocity at each temperature determined from the slope of the straight line. The effect of temperature in the constant of velocity was determined from the linearised Arrhenius equation:

$$\ln k = \ln k_0 - E_a/R/T \quad (4)$$

where  $k_0$  denotes the pre-exponential factor ( $\text{min}^{-1}$ );  $E_a$  denotes the activation energy ( $\text{kcal mol}^{-1}$ );  $R$  denotes the universal gas constant ( $\text{kcal mol}^{-1}\text{K}^{-1}$ ); and  $T$  the absolute temperature ( $^{\circ}\text{K}$ ). The value  $E_a$  was calculated from the slope and  $k_0$  from the intercept of the straight lines given by eqn (4), using a linear regression program.

All the statistical analyses were done using the package STATGRAPHICS version 6.0.

## RESULTS AND DISCUSSION

### Physical and chemical characteristics

The physical-chemical characteristics obtained for double concentrated tomato paste used as sample for the determination of colour kinetics were ( $\pm$  standard deviation):  $^{\circ}\text{Brix}$  ( $20^{\circ}\text{C}$ ) =  $28.1 \pm 0.30$ ; moisture (%) =  $71.9 \pm 0.03$ ;  $a_w$  ( $24^{\circ}\text{C}$ ) =  $0.96 \pm 0.00$ ; acidity (g citric acid/100 g sample) =  $1.49 \pm 0.36$ ; pH =  $3.90 \pm 0.13$ . The values obtained are within the normal range reported in the literature for this product (Goose & Binsted, 1973; Serkat & Luh, 1976; Leoni & Bellucci, 1980; Madaiah *et al.*, 1986; Sandoval *et al.*, 1992).

### Kinetics of colour change during heating

#### Colour parameter 'L'

The results obtained are presented in Fig. 1. This parameter tended to decrease faster during the first 20 min of the heating process, after which the reaction rate

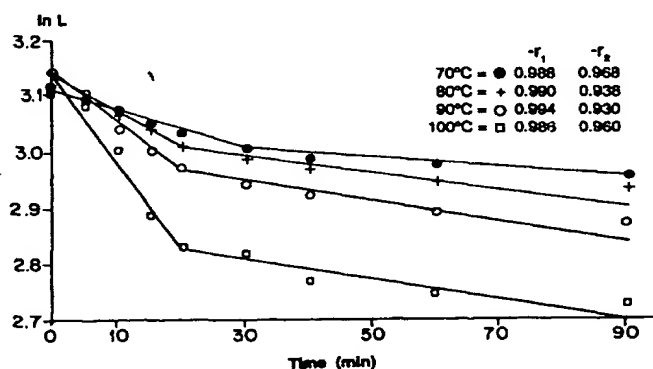


Fig. 1. Kinetics of the thermal degradation of the colour parameter 'L' in double concentrated tomato paste.

became slower. The reaction took place according to two apparent consecutive first order reactions, with linear correlation coefficients ( $-r$ ) between 0.986 and 0.994 for the first phase of the curve and between 0.938 and 0.968 for the second one. In all the cases the analysis of variance showed statistically significant linear regressions ( $p < 0.05$ ).

This behaviour was possibly due to the presence of heat sensitive reactions in the first phase of the curve involving the degradation of thermolabile pigments, which in turn resulted in the formation of dark compounds that reduced luminosity, while in the second phase more thermostable pigments were involved. A similar behaviour was found by Palombo and Wijngaards (1990) in ground meat. The research works done in other products were indicative of simple first order reactions in: pear juice (Petropakis & Montgomery, 1984), sterilised juices (Tanchev, 1985), grape juice (Rhim *et al.*, 1989b), and green olives (Sanchez *et al.*, 1991). However, the above studies were done using relatively longer time intervals and relatively higher temperatures, so that the first phase could possibly not be evidenced in their experiments.

The change in colour during thermal processing of foods is postulated to take place by various mechanisms, including the degradation of pigments, oxidation of ascorbic acid, and the Maillard reaction (Serkat & Luh, 1976; Okitani *et al.*, 1983; Petropakis & Montgomery, 1984). These reactions can take place simultaneously but at a different reaction rate, depending on the colour factor involved, and may explain the two consecutive first order reactions found for this colour parameter. This reaction is actually an apparent first order reaction, since in the colour change there is probably more than one compound or colour factor involved and the reaction does not necessarily take place in one step through a single mechanism.

Figure 1 shows that the velocity constant ( $k$ ) of the reaction, in any phase, increases with an increase in temperature. Values are greater in the first phase than in the second. The dependency of temperature on  $k$  was determined using the linearised Arrhenius eqn (3). The values obtained for the energy of activation  $E_a$  and the pre-exponential factor  $k_0$  are presented in Table 1.

TABLE 1  
Reaction Order and Arrhenius Constants for the Kinetics of Colour Change During Heating of Double Concentrated Tomato Paste

Colour parameter	Reaction order	$E_a$ (kcal mol)	$\ln k_0$ (min <sup>-1</sup> )	(-r)
L (first phase)	1	11.5	11.3	0.996 <sup>b</sup>
L (second phase)	1	5.73	1.28	0.979 <sup>a</sup>
a	1	9.79	9.10	0.983 <sup>b</sup>
b	1	20.5	22.2	0.952 <sup>a</sup>
a/b	1	6.86	5.20	0.986 <sup>b</sup>
$\Delta E$	0	10.2	12.9	-0.977 <sup>a</sup>
SI	1	10.1	9.28	0.989 <sup>b</sup>
Hue angle	1	7.57	5.51	-0.993 <sup>b</sup>

<sup>a</sup>Significant linear regression ( $p < 0.05$ ).

<sup>b</sup>Highly significant linear regression ( $p < 0.01$ ).



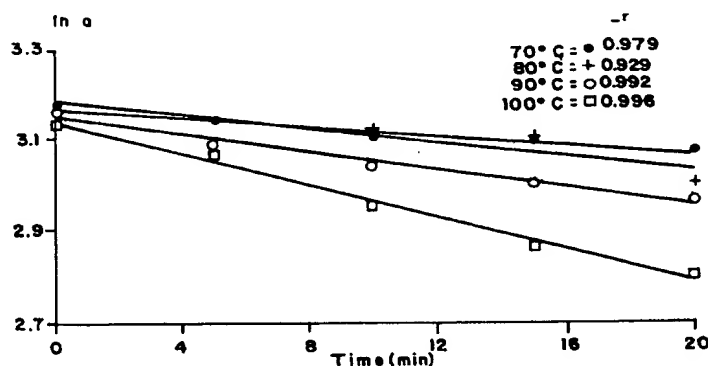


Fig. 2. Kinetics of the thermal degradation of the colour parameter 'a' in double concentrated tomato paste.

#### Colour parameter 'a'

The results for this parameter are shown in Fig. 2. A first order reaction was found. In all the cases a significant ( $p < 0.05$ ) linear regression with correlation coefficients ( $-r$ ) between 0.929 and 0.996 was obtained. A similar behaviour for this parameter was found by other authors in grape juice (Rhim *et al.*, 1989b), green olives (Sanchez *et al.*, 1991), dehydrated tomato juice (Lovric *et al.*, 1980), tomatoes (Bontovits, 1981) and spinach (Schwartz & Lorenzo, 1990, 1991). The results obtained for  $E_a$  and  $k_0$  are shown in Table 1.

Various authors have pointed out that the change in the parameter 'a' in tomato paste, depends basically on the effect of heat on two pigments: lycopene and xanthophyll, which are responsible for the red colour of this product. The colour of the paste depends also on the original chlorophyll content of the juice (Liu & Luh, 1977; Nagle *et al.*, 1979; Moressy & Liverotti, 1982). Red colour degradation with heat in tomato paste is due to the isomerisation of lycopene during heating (Boskovic, 1979), while the chlorophylls degrade to pheophytin, resulting in darkening of the paste (Schwartz & Lorenzo, 1990, 1991).

#### Colour parameter 'b'

The results obtained for the parameter 'b' (Fig. 3) followed a first order reaction. The analysis of variance showed highly significant linear adjustments ( $p < 0.01$ ), with correlation coefficients ( $-r$ ) from 0.902 to 0.995.

Similar results for the order of reaction were found by many authors in dairy products (Burton, 1984; Rhim *et al.*, 1988b) and in pickled green olives (Sanchez *et al.*, 1991). Rhim *et al.* (1988a) found a zero order kinetics in skim milk for this parameter.

The values calculated for  $E_a$  and  $k_0$  are presented in Table 1.

#### Colour parameter 'a/b'

As for the parameters 'a' and 'b', their ratio ('a/b') followed a first order kinetics (Fig. 4). The adjustment to this order showed statistically significant ( $p < 0.05$ ) linear

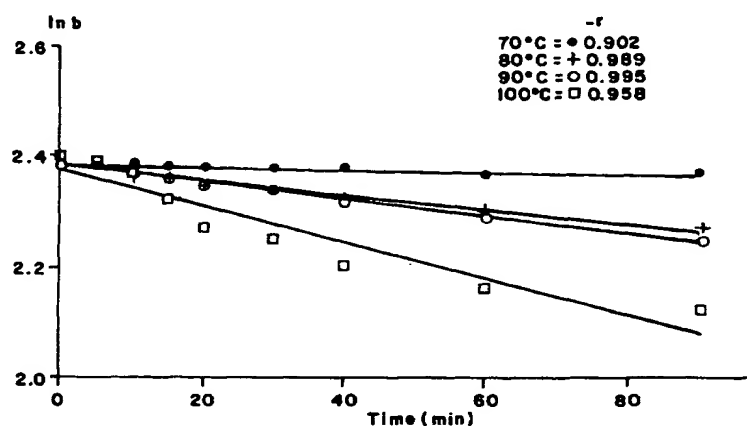


Fig. 3. Kinetics of the thermal degradation of the colour parameter 'b' in double concentrated tomato paste.

regressions with correlation coefficients ( $-r$ ) between 0.880 and 0.987. Likewise, this parameter could be also adjusted satisfactorily to a zero order kinetics as determined by Hayakawa (1977) in green vegetables. The values of  $E_a$  and  $k_0$  obtained from the linearised Arrhenius equation are shown in Table 1.

#### Colour parameter ' $\Delta E$ '

This parameter was calculated from the primary colour parameters using eqn (1). The results obtained are presented in Fig. 5. A zero order reaction for the effect of

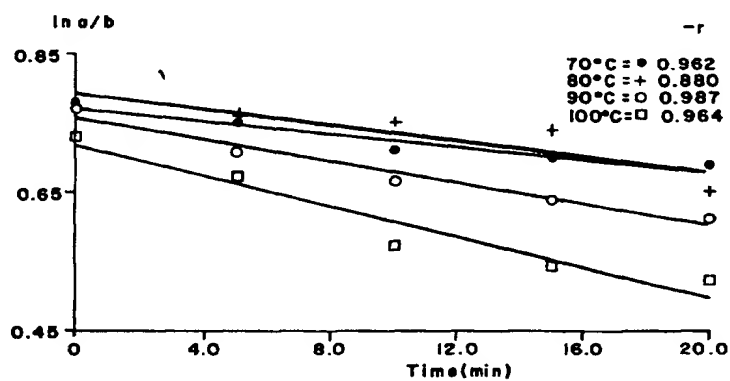


Fig. 4. Kinetics of the thermal degradation of the colour parameter 'a/b' in double concentrated tomato paste.

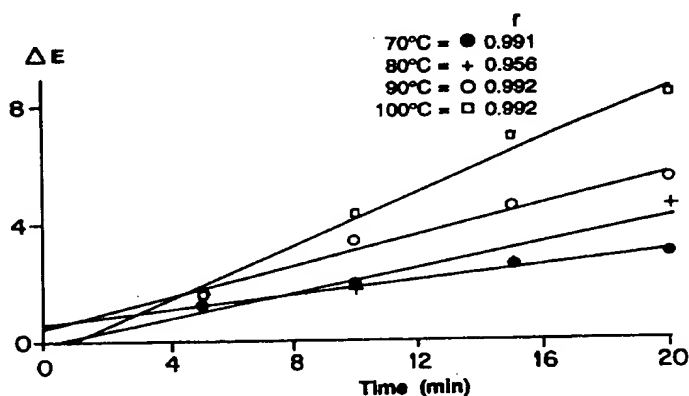


Fig. 5. Kinetics of the thermal degradation of the colour parameter ' $\Delta E$ ' in double concentrated tomato paste.

heat in this parameter was determined. The same order of reaction was found by Flora (1976) and Rhim *et al.* (1989b) in grape juice, and by Pagliarini *et al.* (1990) in milk. Colour difference increased with temperature. A similar behaviour in other food products was reported by other authors: dairy products (Rhim *et al.*, 1988a; Pagliarini *et al.*, 1990), and grape juice (Rhim *et al.*, 1989b). The analysis of variance showed significant linear adjustments to this kinetic model ( $p < 0.05$ ) with linear correlation coefficients ( $r$ ) between 0.956 and 0.992. The  $E_a$  and  $k_0$  values obtained from the Arrhenius equation are presented in Table 1.

#### Colour parameter 'SI'

The saturation index (SI) was calculated from values ' $a$ ' and ' $b$ ' using eqn (2). This parameter diminished as the temperature increased and showed a first order kinetics (Fig. 6). Similar behaviour was observed by Rhim *et al.* (1989b) in grape juice. The linear adjustment to this kinetic model showed significant ( $p < 0.05$ ) values in all cases, with linear correlation coefficients ( $r$ ) between 0.936 and 0.998. The values of  $E_a$  and  $k_0$  are shown in Table 1.

#### Hue angle

The Hue angle followed a kinetics behaviour similar to that of the parameter ' $a/b$ '. It increased with temperature and time, showing a first order kinetics (Fig. 7). The adjustment to this order showed statistically significant ( $p < 0.05$ ) linear regressions with correlation coefficients ( $r$ ) between 0.890 and 0.980. As for ' $a/b$ ' this parameter could be also adjusted satisfactorily to a zero order kinetics. The values of  $E_a$  and  $k_0$  obtained from the linearised Arrhenius equation are shown in Table 1.

From the data presented above for the colour parameters studied, it can be observed that the total colour difference  $\Delta E$  showed the highest value for the rate constant ( $k$ ), calculated with eqn (4) as compared with the other colour parameters, thus showing the greatest rate of change at a given temperature. According to the

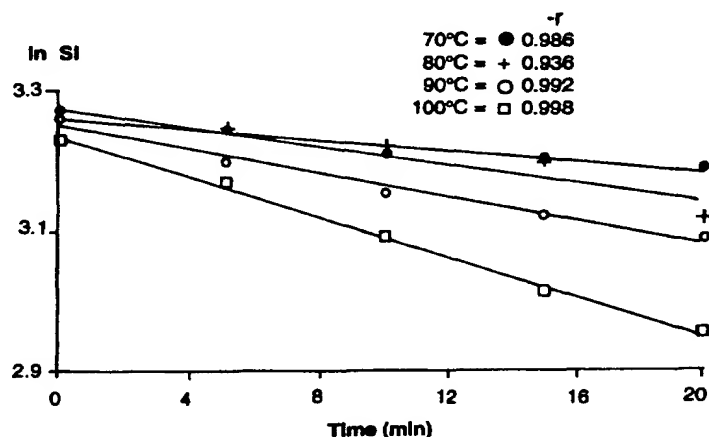


Fig. 6. Kinetics of the thermal degradation of the colour parameter 'SI' in double concentrated tomato paste.

experimental data obtained, the reaction rate for the colour parameters studied can be arranged in decreasing order at a given temperature. For example at 100°C the rate constant ( $k$  in  $\text{min}^{-1}$ ) was:  $\Delta E$  (0.458), 'a' (0.0172),  $L$  (first phase) (0.0150), SI (0.0144), 'a/b' (0.0110), Hue angle (0.00924), 'b' (0.00321) and  $L$  (second phase)

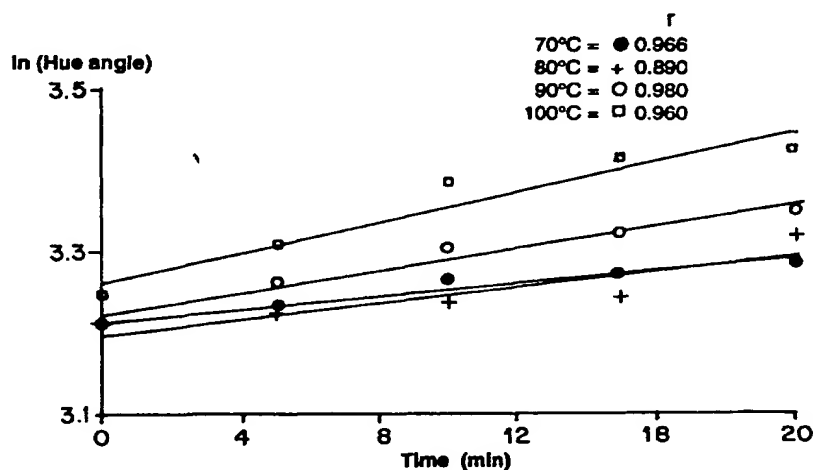


Fig. 7. Kinetics of the thermal degradation of the colour parameter 'Hue angle' in double concentrated tomato paste.

(0.00146); while at 70°C the order was:  $\Delta E$  (0.122), 'a' (0.00500), 'a/b' (0.00460), SI (0.00406), Hue angle (0.00384),  $L$  (first phase) (0.00360),  $L$  (second phase) (0.000762) and 'b' (0.000240). These differences between the relative magnitudes of the reaction rate of the colour parameters studied at lower and higher temperatures can be explained by the sensitivity of the reaction constant to changes in temperature given by the term  $E_a$  in eqn (4). From all the parameters studied, 'b' showed the highest  $E_a$  (20.5 kcal mol), and therefore was the most sensitive to changes in temperature, although its rate constant was among the lower.  $L$  (second phase) and 'a/b' showed  $E_a$  values of 5.73 and 6.86 kcal mol, among the less sensitive to changes in temperature.

### CONCLUSIONS

The kinetic study of the colour change of double concentrated tomato paste during heating at temperatures between 70.0 and 100.0°C, showed that all the colour parameters investigated ('L', 'a', 'b', 'a/b', SI and Hue angle) followed a first order reaction kinetics during heating, with the exception of the parameter  $\Delta E$  that followed a zero order kinetics. The colour parameter 'L' changed according to two consecutive apparent first order reactions with values of  $E_a$  of 11.5 and 5.73 kcal mol and  $\ln k_0$  of 11.3 and 1.28 min<sup>-1</sup> for both phases, respectively, and a breaking point after 20 min of heating. The 'a/b' ratio and the Hue angle could also be adjusted to a zero order kinetics.

The values of  $E_a$  and  $k_0$  obtained for the colour parameters studied in this research work (Table 1), allows the prediction of colour changes that take place in double concentrated tomato paste during thermal processing.

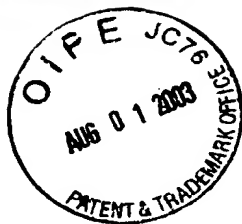
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# **WHITE BOOK ON THE ANTIOXIDANTS IN TOMATOES AND TOMATO PRODUCTS AND THEIR HEALTH BENEFITS**

**Final report of the Concerted Action FAIR CT97-3233**

Editor:  
AMITOM, BP 235, 84010 Avignon Cedex 1, France  
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## **Effects of mechanical and thermal treatments and storage conditions on antioxidants content and their bioavailability in processed tomatoes**

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3	thermal stabilisation treatments	D I	Avoid fouling in heat exchangers Reduce holding time if not necessary Use temperature as low as possible
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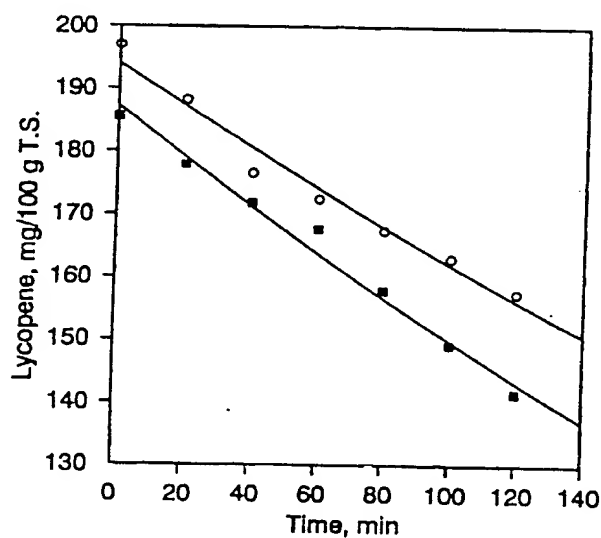
### *Survey of references:*

The frequently cited studies by Cole and Kapur do not refer to industrially processed products, since they study degradation with the lycopene dissolved in an organic solution. Results show the importance of temperature in the breakdown of lycopene by oxygen, but in experimental conditions, different from those used in industrial processing. Important losses were observed, but with lycopene in organic solutions. In their pioneer study on the stability of lycopene, Cole and Kapur (1957a, 1957b) investigated the degradation of lycopene extracted from tomatoes by heating hexane and light petroleum ether lycopene solutions at 65° and 100°C under a slow current of oxygen. The effects of the presence of copper (copper stearate 1 mg/L) were also investigated. Lycopene was determined by spectrophotometric analysis, and oxidation products were separated by paper chromatography.

In pure solution, apparent lycopene losses of 26% and 35% were recorded after 3 h at 65 °C and 100 °C respectively. Lycopene degradation was at an almost constant rate at 100 °C, while an induction period was observed at 65 °C. The presence of copper increased lycopene loss in the above-mentioned conditions to 54% and 88.5% respectively. In the same study, the authors studied lycopene degradation due to heating of serum-free tomato pulp. Products were heated at 100 °C, under oxygen or CO<sub>2</sub> flux for up to 3 h, both in the dark and in the light. Lycopene apparent loss was slightly higher in the daylight, and equal to 11.35 and 33.1%, under CO<sub>2</sub> and oxygen respectively. The effects of increasing temperature and increasing light intensity were also investigated. Both light intensity and temperature influenced the rate of lycopene loss, and the effect of increasing temperature was particularly marked. Lycopene loss after 3 hours' heating under oxygen was 18.9%, 34.9% and 53.9% at 60°, 100 and 110 °C (all trials with 100 ft. candle light intensity). Some lycopene degradation products were detected, such as acetone, methyl-heptenone, laevulinic aldehyde and a  $\alpha$ -carbonyl, probably glyoxal. From these first studies, it was concluded that lycopene is quite sensitive to heat treatments in the presence of oxygen. It also appeared that in these conditions (soluble form) the food matrix did not provide a protective effect against lycopene oxidative degradation.

During the heating of tomato pulp at 100°C for 120 min at atmospheric pressure, Sharma and Le Maguer (1996a) found that the lycopene content in pulp decreased from 185.5 to 141.4 mg/100 g of d.w. (equation of pseudo first order, with an apparent reaction rate constant  $K$  of 0.0023 min<sup>-1</sup>). The experimental values suitably followed the fitted data (Figure 1) with residual mean sum of squares (RMSS) less than 0.1%

The experimental conditions were very severe and far from the ones used in a usual industrial process.



$$L = L_o \times [\exp(-Kt)]$$

$L$  = amount of lycopene at time  $t$ , mg/100 g TS

$L_o$  = initial amount of lycopene, mg/100 g TS

$K$  = apparent reaction rate constant, min<sup>-1</sup>

$t$  = time of heating, min

Fig. 1 - Decrease in lycopene content in pulp during heating.

Nicoli *et al.* studied the effect of heat treatment on the complex of global antioxidant properties of a tomato juice. The information is aggregate and non-specific for lycopene. After 50 hours at 95°C, the antioxidant property of the juice was practically unaltered, and the authors hypothesize the formation of a compound with novel antioxidant properties (MRP). The lack of data relating to carotenoid concentrations renders the study invalid for the evaluation of the effect of heat treatment on the degradation of lycopene

Similar results were obtained regarding the Lerici *et al.* study

Zanetti studied the global effect of the industrial process. For the cold break production of concentrate manufactured under aseptic conditions and thus using medium-intensity heat treatments in the initial stages (extraction of the juice and concentration), becoming more intensive in the final stage, that of stabilisation, a 28% reduction of lycopene was obtained (with reference to the t.s. content.) as against a 38%  $\beta$ -carotene loss and a 49% phytoene loss.

In the case of diced tomato, no decrease was observed in the case of a filling under aseptic conditions (heating to a high temperature, but for relatively short times and with immediate cooling), or in a hot filling into 500 g cans (bulk heating and quite rapid cooling), whereas there was a decrease of around 10% in the case of a filling into 5 kg cans (slow and prolonged heating of the already canned product and slower cooling).

### *Comments and topics*

The kinetics of lycopene degradation in an aqueous matrix is extremely slow and thus the rise in temperature which occurs during pasteurisation treatments does not cause significant reductions in lycopene content. The decline in quality (colour) is greater than the lycopene decrease, and this is probably due to the fact that the part which degrades is the outer surface of the coagula, i.e. that which is most exposed to the action of the oxidative agents, but also that which is responsible for the "visible" effect of pigmentation.

### *Is this step an RCPL ?*

Q1	Q2	Q3	Q4	result
Yes	Yes			Yes

9	Evaporation ( puree, paste)	D	Avoid fouling
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### Survey of references

In general, data are reported which reveal the values of lycopene in fresh tomato and in concentrates. Unfortunately, the products are hardly ever comparable, either because the fresh tomato is not the same as that utilised for the concentrate or because the concentration ratios are not fixed, or else because measurements are taken of all the processes and not only at the concentration stage. It must, however, be borne in mind that the concentration by evaporation occurs under vacuum and at temperatures lower than those utilised at the breaking and stabilisation stages, albeit for greater times.

Abushita *et al.* (2000) evaluated the changes in carotenoids and antioxidant vitamins (ascorbic acid and tocopherols) in tomatoes during industrial tomato paste production. Products were sampled and analysed (solvent extraction followed by HPLC determination) at 3 processing stages: raw tomato, crushed-sieved puree, and pasteurised paste (28°Bx). The authors observed an increase in the *all-trans* lycopene and total carotenoid content (on a dry weight basis) during processing, which was ascribed to the removal of seeds and other by-products. *All-trans*  $\beta$ -carotene concentration decreased from 37.2 in raw tomatoes to 26.3 mg/kg d.w. in tomato paste, while *cis*  $\beta$ -carotene increased (from <1 to 9.7 mg/kg d.w.). In contrast, no lycopene isomerisation was observed (*cis* lycopene accounted for 1.7% and 1.5% total lycopene in raw tomatoes and tomato paste respectively). With regard to other vitamins, tomatoes lost about 38% of their original ascorbic acid content during hot-break extraction (90°C for 5-10 min), and a further 16% loss was caused by concentration (60-70°C for 4 h). Tocopherols were not affected by hot-break extraction, but  $\alpha$ -tocopherol decreased by 20%,  $\alpha$ -tocopherol quinone by 46% and  $\gamma$ -tocopherol by 33% during the thermal processing of tomato paste. The authors concluded that lycopene was stable during tomato paste processing, whereas  $\beta$ -carotene and other antioxidant vitamins were lost to a considerable extent.

Liu and Luh studied the total effect of paste processing (pilot plant), starting from tomatoes at different stages of ripeness. Unfortunately, they did not report the carotenoid contents of raw material and limited the analyses to the pastes obtained.

The data reported by Tavares and Rodriguez-Amaya are not utilisable either, since they compare the carotenoid content in fresh tomatoes and in industrially produced derivatives taken from outlet shelves; besides, they do not specify the dry weight values at all. The same consideration must be made for the study by Rao *et al.* (1998) and for that of Tonucci *et al.* ,

who reported the aggregate result of processing. Again, it was observed that fresh and differently processed tomatoes contained the same carotenoid compounds with the exception of lutein, which was not detected in ketchup and tomato sauce. Since the data were expressed on a fresh weight basis and solid content was not given, it is only possible to compare quantitative ratios of the individual components in the various products. These ratios did not vary significantly for processed products and whole fresh tomatoes (with the exception of lutein, as previously mentioned), indicating that processing did not cause important degradation of carotenoids. Isomerisation of carotenoids was not investigated in this work. The lycopene content ranges from 93 ppm in fresh tomatoes to 167 in puree and 555 in paste, although the d.w. values are not reported. Normally, the paste/fresh concentration ratio is 6 (the same as that between the content of paste and fresh tomatoes,).

The thesis by Zanetti yields a datum that can be utilised in part. In the production process of HB double concentrate, he observed a progressive lycopene reduction (with reference to 1 kg of dry weight) from 3.7 g (juice at 7 °Brix prior to concentration) to 2.75 (concentrate 24 °Brix), which he attributes to the concentration phase by evaporation, but which is also influenced by the heat stabilisation stage (aseptic packaging)

#### *Comments and topics*

Evaporation would not appear capable of causing reductions in the lycopene content higher than those due to heat treatments in general. The prevention of fouling allows for quicker operating times and thus reduces the possibility of heat damage to the lycopene

*Is this step an RCPL ?*

Q1	Q2	Q3	Q4	result
No	No	No		No

## 2. Heat damage and antioxidant power

When evaluating the effects of heat treatments on the antioxidant activity of tomato products, the formation of Maillard reaction products must also be considered. HMF and furosine ( $\epsilon$ -N-(2-furoyl-methyl-L-lysine) formation in heat-treated tomato products has been studied by Hydalgo *et al.* (1999). In this study, HMF and furosine reaction kinetics were examined in four tomato products with differing dry matter content (from 10.2 to 34.5%) over a temperature range of 80-120°C. The reactions followed a pseudo-zero-order kinetics;  $E_a$  values were 139.9 kJ/mol for HMF and 93.9 kJ/mol for furosine formation. Furosine concentration was also determined in many commercial products (detecting values from 43 to 140 for tomato pulp, from 93 to 132 for tomato sauce, and from 220 to 468mg/100 g protein for tomato paste) and during the industrial production of tomato pulp and paste (Hydalgo *et al.*, 1998). This study led to the conclusion that furosine can represent a sensitive heat damage index in tomato products. The interest in Maillard reaction products is due to their activity as pro-oxidant and antioxidant compounds.

Anese *et al.* (1999) studied the antioxidant properties of tomato juice as affected by heating (70° or 95°C for up to 50 h). The antioxidant activity was measured as peroxyl radical quenching and oxygen scavenging activity. A decrease in the antioxidant potential was found for short heat treatments; this decrease was ascribed to both degradation of natural antioxidant components (such as ascorbic acid) and the formation of early Maillard reaction products with pro-oxidant properties. However, prolonged heating caused a recovery of the initial antioxidant activity and then an increase in the overall antioxidant activity. This was ascribed to the formation of melanoidins, which exert antioxidant activity during the advanced steps of the Maillard reaction.